PRODUCTION OF HYDROGEN ENRICHED SYN-GAS BY ABSORPTION METHOD

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BY

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CERTIFICATE

This is to certify that the thesis entitled **"PRODUCTION OF HYDROGEN ENRICHED SYN-GAS BY ABSORPTION METHOD"** submitted by Sagar Sourav (108CH040) in partial fulfillment of the requirement for the award of BACHELOR OF TECHNOLOGY Degree in Chemical Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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ABSTRACT

Hydrogen-enriched syngas, HESG, addresses two dominant energy and environmental issues: decarbonization and improved energy management. Reducing the CO_2 content of syn-gas widens our efforts to build a bridge to an ultra-low carbon world. With HESG, it becomes possible to reduce emissions, improve the efficiency of end-use equipment, and lower the overall carbon intensity of syngas in the years to come. Higher CO_2 content in the syngas also lowers the calorific value. This work is aimed at reducing the CO_2 content in the syngas by absorption process. For this purpose we have taken the help of ASPEN PLUS simulator. The rate-based non-equilibrium, RateFrac, model is used for column design. Mono ethanolamine (MEA) is taken as liquid solvent and various parameters like flow rate and temperature of the solvent and number of segments of the absorption column were varied to test the CO_2 absorption efficiency of the solvent. Similarly CaO absorption efficiency was found by experimental methods for gasification process carried out under different conditions like variation in temperature, equivalence ratio and steam to biomass ratio. The efficiency was found to be less than 30% due to ineffective fluidization.

Key Words: ASPEN PLUS Simulator, Hydrogen Enriched Syn-gas, Absorption

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CHAPTER-1
INTRODUCTION

The future of oil-derived fuels, such as gasoline and diesel for use in the transportation and energy sectors, is unknown. In addition to declining crude oil supplies and political instability in the regions with large oil reserves, strict emission regulations are creating a need for alternative fuels. One of these alternative fuels, hydrogen, has the highest specific energy content of all conventional fuels and is the most abundant element in the universe. When it is used in a fuel cell, internal combustion (IC) engine, or turbine, the end result is near pollution-free energy with water as the main by-product. Another advantage of hydrogen as an energy carrier is its flexibility. Localized production of hydrogen is feasible nearly everywhere from several sources (fossil fuels, biomass, water, etc.). Also, it can be used for power generation, as a key ingredient in liquid hydrocarbon fuels produced via Fischer–Tropsch synthesis, and as a chemical feedstock for ammonia synthesis and hydrogenation processes. The problem with hydrogen lies in the fact that it is not found in its elemental form on earth, but rather as a component of raw materials, making it a secondary energy carrier. Several methods are available for production of hydrogen, but many of these processes are restricted to laboratory scale only.

Hydrogen can be produced from a variety of feed stock. These include fossil resources, such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources (*e.g.* sunlight, wind, wave or hydro-power). A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical. Each technology is in a different stage of development, and each offers unique opportunities, benefits and challenges. Local availability of feed stock, the maturity of the technology, market applications and demand, policy issues, and costs will all influence the choice and timing of the various options for hydrogen production. The various methods available for hydrogen production are

- H_2 from fossil energy sources.
- H_2 from biomass.
- Photo-electrolysis (photolysis).
- Photo-biological hydrogen production.

We will restrict our discussion to only production from biomass by gasification process (and further enrichment), where by a H_2, CO, CO_2, CH_4 mixture is produced referred to as syngas.

Biomass is converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds by applying heat under pressure in the presence of steam and a controlled amount of oxygen(or air) in a unit called a "Gasifier". The biomass is broken apart chemically by the gasifier's heat, steam, and oxygen, setting into motion chemical reactions that produce a synthesis gas, or "syngas"—a mixture of primarily hydrogen, carbon monoxide, and some amount of carbon dioxide. The carbon monoxide then reacts with water to form carbon dioxide and more hydrogen (water-gas shift reaction).

Simplified Example of Gasification Reaction

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species} \quad (1.1)$$

Water-Gas Shift Reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (+small amount of heat)} \quad (1.2)$$

High to ultra-high purity hydrogen may be needed for the durable and efficient operation of fuel cells, consumption in different process plants, in semiconductor industry and as an energy carrier. Impurities are believed to cause various problems in the current state-of-the-art fuel cell designs, including catalyst poisoning and membrane failure. As such, additional process steps may be required to purify the hydrogen to meet industry quality standards.

In general, biomass does not gasify as easily as coal, and it produces other hydrocarbon compounds in the gas mixture exiting the gasifier. As a result, typically, an extra step must be taken to reform these hydrocarbons with a catalyst to yield a clean syngas mixture of hydrogen, carbon monoxide, and carbon dioxide. Then, just as in the gasification process for hydrogen production, a shift reaction step (with steam) converts the carbon monoxide to carbon dioxide. The hydrogen produced is then separated and purified (or enriched).

The objective of this project is to produce hydrogen enriched syn-gas. This purpose can be achieved by two methods- liquid solvent absorption and solid sorbent absorption.

CHAPTER-2

LITERATURE REVIEW

2.1 Hydrogen Purification

Several techniques have been developed for purification of hydrogen. These fall broadly into three categories.

- Chemical-
  - Catalytic Purification
- Physical -
  - Metal Hydride Separation
  - Pressure Swing Adsorption
  - Cryogenic Separation.
- Selective Diffusion (Membrane Separation)-
  - Noble Metal Membrane Diffusion
  - Polymer Membrane Diffusion
  - Ceramic Membrane Diffusion
  - Porous Carbon Diffusion

2.1.1 Chemical separation

2.1.1.1 Catalytic Purification

Catalytic purification is mainly used for removal of traces of oxygen which might be present in the syngas as unburned air. In this process the removal of oxygen from gas mixture is done by causing its catalytic combination with hydrogen to form water. The concentration of oxygen in such gas stream is too low to permit free combustion of hydrogen, but the reaction can be made to go readily in the presence of suitable catalyst. Among the readily available catalyst materials for water synthesis copper appears to be the most promising.

Different catalyst such as (1) Copper shot, (2) Copper reduced from Baker and Adamson C.P. granular copper oxide, (3) Copper reduced from fused copper oxide which was prepared by heating copper in an oxidizing atmosphere with an oxidizing flame are tested by J. A. Almquist and E. D. Crittenden and nearly 70-80% removal of oxygen was observed [1].

2.1.2. Physical separation

2.1.2.1. Metal hydride Separation

Many kinds of metals or alloys can react reversibly with a large amount of hydrogen under certain conditions. The products of the forward reaction are called metal hydrides (MH), and the reaction can be written as

$$M + (x/2)H_2 \rightarrow MH_x + \text{heat} \quad (2.1)$$

For the isothermal reaction process phenomenon will occur for the equilibrium pressure in the system. Metal hydride absorbs and releases hydrogen in an equilibrium process according to the designed alloy temperature and pressure. When it is maintained at an equilibrium temperature it will not affect the hydrogen maintaining pressure, and it keeps the absorbed amount of hydrogen. On the other hand, when the pressure in a system falls because hydrogen is extracted, the metal hydride releases hydrogen in order to keep the equilibrium pressure.

The process consists of the following main steps [2]

- Impure hydrogen flows into the reactor. The hydrogen is selectively absorbed by the metal hydride powder in an exothermic reaction. The reactor is cooled. The nitrogen accumulates in the void with increasing concentration in the direction of the gas flow.
- Impurities are removed from the reactor by purging it with pure hydrogen.
- The hydrogen pressure in the reactor is increased by heating the metal hydride powder.
- The metal hydride powder is degassed by supplying further heat and pure hydrogen is given off.

2.1.2.2. Pressure Swing Adsorption

Pressure swing adsorption processes rely on the fact that under pressure, gases tend to be attracted to solid surfaces, or “adsorbed”. The higher the pressure, the more the gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. PSA processes can be used to separate gases in a mixture because different gases tend to be attracted to different solid surfaces more or less strongly. If a gas mixture such as H_2 and CO_2, for example, is passed under pressure through a vessel containing an adsorbent bed that attracts H_2 more strongly than it does CO_2, part or all of the H_2 will stay in the bed, and the gas coming out of the vessel will be enriched in CO_2.

When the bed reaches the end of its capacity to adsorb H_2, it can be regenerated by reducing the partial pressure, thereby releasing the adsorbed H_2. Partial pressure reduction can be accomplished by lowering the total pressure or using a purge gas.

Due to the availability of large surface area, usually porous materials are chosen as adsorbent. Typical adsorbents are activated carbon, silica gel, alumina and zeolite.

One of the major industrial applications of PSA is hydrogen production from various gas sources. The typical industrial systems designed by Golden and Sircar can produce 99.99+% pure H_2products with a recovery of 86% [3].

To improve the separation quality multi-bed PSA process for the simultaneous production ofpure H_2 and CO_2 had been designed. Such process can produce a primary H_2 product at a purity of 99.999% and recovery of 87.1% while simultaneously producing secondary CO_2 product at a purity of 99.4% with a recovery of 94% [3].

2.1.2.3. Cryogenic Separation

Separation of hydrogen gas from a mixture of hydrogen containing gas is done by liquefaction of the higher boiling component. The basic process consists of cooling the gas stream to condense out all components except hydrogen. The removal of CO can be enhanced by washing the gas with liquid methane or liquid nitrogen. The use of the nitrogen is particularly effective when the product gas is to be used for ammonia synthesis since 75% hydrogen and 25% nitrogen is required .The basic types of cryogenic processes used for producing purified hydrogen from impure gas stream are listed in Table-1 [4].

Table-1 Different cryogenic processes for hydrogen purification

Type of process	Products	Purity (%)	Recovery (%)
Condensation	Hydrogen	98	90-95
Condensation and CH_4/CO separation	Hydrogen Carbon monoxide	98 99.8	90-95 95
Methane wash	Hydrogen Carbon monoxide	99 98	99
Nitrogen wash	3:1 H_2:N_2 mixture	99	99

2.1.3. Selective diffusion

Most hydrogen separation membranes operate on the principle that only hydrogen can penetrate through the membrane because of the inherent properties of the material. The mechanism for hydrogen penetration through the membrane depends on the type of membrane in question. Most membranes rely on the partial pressure of hydrogen in the feed stream as the driving force for permeation, which is balanced with the partial pressure of hydrogen in the product (permeate) stream.

Table-2 [5] compares, in general, the relative operational performance of five membrane types. Each membrane has its own advantage and disadvantage and research is being carried out to develop better version of each.

Table-2 Different types of membrane used for hydrogen separation [5]

	Dense Polymer	**Micro-porous Ceramic**	**Dense Ceramic**	**Porous Carbon**	**Dense Metallic**
Temperature Range	<100^{o}C	200-600^{o} C	600-900^{o} C	500-900^{o} C	300-600^{o} C
H_2 Selectivity	Low	Moderate	Very High	Low	Very High
H2 Flux	Low	High	Moderate	Moderate	High
Known Poisoning issues	HCl, $SO_{x,}$ CO_2		H_2S	Strong Vapors, Organics	H_2S, HCl, CO
Example materials	Polymers	Silica, Alumina, Zirconia, Titania, Zeolites	$SrCeO_{3,}$ $BaCeO_3$	Carbon	Palladium Alloys Pd-Cu Pd-Au
Transport Mechanism	Solution/ Diffusion	Molecular Sieving	Solution/Diffusion	Surface Diffusion, Molecular Sieving	Solution/ Diffusion

Hydrogen separation membrane technologies have the potential to play an important role in near-zero-emission plants because membranes can produce hydrogen economically, at large scale, and with very low levels of impurities.

2.2. CO_2 Capture by Absorption

Several techniques for H_2purification (from syngas) and their comparative efficiencies are discussed in the last section. Ultrapure H_2 production involves additional cost and performance penalties. However the requirement of H_2 in such purity and their vast utilization in different process plants suppresses these drawbacks.

But in our research project we are interested in production of hydrogen enriched syngas. Large scale industrial application of this technology is done by utilizing the gas as a fuel in different sections (such as boiler) of a process plant. To meet such a requirement there is no need in purifying syngas to such an extent. Only CO_2 removal will do the job, as the CH_4 or CO present in small quantities are also combustible and will not alter the heating value of the gas significantly. Again it is much more cost effective in comparison with its final use. Hence our aim for this research project is the pre-combustion capture of carbon dioxide, which can be done by simple absorption processes.

2.2.1 Pre-combustion capture of CO_2

Pre-combustion capture of CO_2 gas comprises gasification of biomass with air under pressure followed by CO_2 removal using AGR (acid gas removal) process. The resulting hydrogen rich syngas is then supplied to the boiler section or gas turbine power block.

The oil, gas and chemical industries have been separating $CO_2$from gas streams for decades at commercial scale. However, to date, none of the IGCC (Integrated Gasification Combined Cycle) plant in operation in several countries has incorporated CO_2 capture [7].

There are different methods available for CO_2 capture such as (1) liquid solvent absorption and (2) solid sorbent absorption.

2.2.1.1. Liquid Solvent Absorption

Current commercially available pre-combustion CO_2capture processes are based on the use of solvents. There are two major generic types of CO_2removal solvents for pre-combustion capture – chemical and physical. Typically all the solvents can accomplish greater than 90 per cent CO_2 removal [7].

In this process liquid chemicals are used to absorb the CO_2 and then release it at an elevated temperature in another vessel. The process [8] can be briefed as follows.

- After the gasification of biomass the gas enters the absorption column. There it comes into contact with the solvent which absorbs the CO_2. The hydrogen rich syngas leaves the absorption column at the top (and then supplied to the gas turbine or the boiler section), and the rich solvent containing the CO_2 is then pumped to another column called a stripping column.
- The rich solvent is then heated to about 120°C, causing the CO_2 to be released from the solvent. The CO_2 emerges at the top of the stripper column where it is cooled, allowing the removal of water and traces of solvents. The liquid is returned to the top of the stripper column and the lean solvent is pumped from the bottom back to the absorber.
- On the way, the hot, lean solvent passes through a heat exchanger, along with the rich solvent leaving the absorber column. This cools the lean solvent, ready for more CO_2 absorption, and heats the rich solvent on its way to the stripper column. The solvent can be used over and over again to perform the separation of CO_2.

Thus by this process one can obtain pure CO_2 gas along with hydrogen rich fuel gas.

The CO_2 absorption efficiency of common alkanolamines like monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) was evaluated by Amornvadee Veawab, Adisorn Aroonwilas, and Paitoon Tontiwachwuthiku [9] for two different CO_2 loading and their observations have been presented in Fig-1.

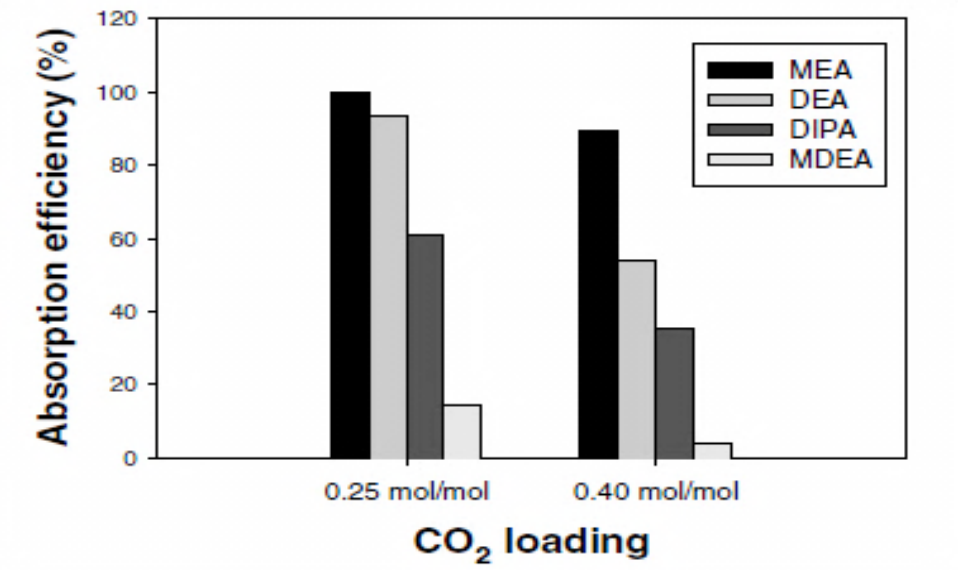

Figure-1 Absorption efficiency of different amine solutions [9]

2.2.1.2. Solid Sorbent Absorption

Absorption of CO_2 on solid sorbent is a chemical process. In most of the processes the gas to be CO_2freed is passed through a packed bed of solid sorbent, where the CO_2 gas reacts with the sorbent and converted to another product and CO_2 free gas passes through the column. When the absorbing capacity of the packed bed reaches the end point the gas flow is stopped and the bed material is recovered by another reaction, where by CO_2 gas is removed by simple heating [10].

The objective of the study is to identify and evaluate novel sorbents that potentially could be utilized in a dry, regenerable scrubbing process for the capture of CO_2 from gaseous streams. Of particular interest are sorbents containing alkali- and alkaline-earth metals distributed onto a substrate support. Specifically, potassium carbonate and calcium oxide are the subjects of the experimental investigations. The chemical reactions for CO_2 capture using these compounds are shown in reactions 1 and 2. The forward reaction path depicts absorption of CO2, whereas regeneration is expressed as the reverse reaction path.

$$K_2CO_3 + CO_2 + H_20 \rightarrow 2KHCO_3 \quad (2.2)$$

$$CaO + CO_2 \rightarrow CaCO_3 \quad (2.3)$$

The use of alkali- or alkaline-earth metals for CO_2 capture has been previously reported in the literature. Work by Japanese researchers encompassed the potential use of potassium, sodium, and lithium compounds as CO_2 sorbents. Potassium carbonate was emphasized as a good candidate while utilizing an activated carbon as the substrate material. Earlier studies by the same researchers examined the use of other substrate materials, including silica gel, alumina [11].

The use of potassium carbonate [11], in addition to other alkali-metal materials, was studied by the space agency (NASA) as a regenerative means by which to absorb CO_2 and H_2O. The intent was to develop portable life support systems to scrub breathing air during human space travel. Japan, in conjunction with development of the space station with NASA, also pursued regenerable solid sorbents for space travel using a solid amine.

In other work, silver was used to capture CO_2 [11]. The unsupported solid sorbent was composed of silver carbonate in a combination of alkali metal silicate (sodium and/or potassium), alkali metal carbonate (cesium, potassium and/or sodium), and an alkaline earth metal salt (nitrates and chlorides of calcium, magnesium, and/or barium).

The use of calcium, an alkaline earth metal [11], for CO_2 capture in a dry, regenerable sorbent process, has been proposed in prior studies. The carbonation reaction is employed in the CO_2 Acceptor Process developed several decades ago for coal gasification. A summary of the process describes the gasification of coal by steam. The energy required for gasification is partially supplied by the exothermic carbonation reaction of dolomitic lime. Of more recent notable interest is a series of papers by several investigators. The effects of temperature, pressure, and reactive gas composition on the gas-solid reaction were examined in an electro balance reactor. Multi-cycle tests were conducted to demonstrate the durability of the material. Some degradation of the material was observed during multi-cycle tests. Calcined dolomite, a mixture of $CaCO_3$ and $MgCO_3$, proved to be superior in performance to calcined $CaCO_3$. It should be noted that these studies were conducted using fine, unsupported, powdered materials. Thus far we have reviewed about the bed material that has got good potential for CO_2 absorption. Now we will look into some of the particular bed materials in detail.

CO_2 absorption by sodasorb:

Sodasorb absorbent is a proprietary mixture of calcium hydroxide, sodium hydroxide, potassium hydroxide and water. In sodasorb absorption the CO_2 first reacts with water to form carbonic acid, subsequently reacting with the hydroxides to form soluble salts of both sodium and potassium carbonate. The soluble salt then reacts with calcium hydroxide to form insoluble calcium carbonate. By products include both heat and water.

Neutralisation of CO_2 may be expressed as the following equations

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (2.4)$$

$$2H_2CO_3 + 2NaOH + 2KOH \rightarrow Na_2CO_3 + K_2CO_3 + 2H_2O + \text{heat} \quad (2.5)$$

$$2Ca(OH)_2 + Na_2CO_3 + K_2CO_3 \rightarrow 2CaCO_3 + 2NaOH + 2KOH + \text{heat} \quad (2.6)$$

In a properly packed well designed column [12], approximately 100g of sodasorb will absorb 15L of CO_2.

Dry Potassium Based Sorbent:

Potassium-based sorbents were prepared by impregnation with potassium carbonate on supports such as coconut activated charcoal (AC1), coal active carbon (AC2) and activated alumina (Al_2O_3).Sorbents such as K_2CO_3/AC1, K_2CO_3/AC2, and K_2CO_3/Al_2O_3 showed excellent carbonation capacity and a total conversion of 89.2, 87.9, and 87.6%, respectively, in the fluidized-bed test [13].

CHAPTER-3

DESCRIPTION OF MODEL, SIMULATION AND EXPERIMENTATION

ASPEN PLUS simulator provides an opportunity to check the feasibility of a process, to study and investigate the effect of various operating parameters on various reactions. It is a strong tool for simulation studies and helps in analyzing the outcome of a process.

3.1 ASPEN PLUS Simulation

The most actual method for CO_2 removal is by absorption in an amine based solvent. For this purpose different models are available in ASPEN PLUS simulator. All these models can be divided into two main categories, Equilibrium Models and Rate-Based Non-Equilibrium Models. The Equilibrium Model assumes each tray or unit to be ideal and based on this assumption it simulates the process. Non-Equilibrium Model performs an initialization calculation where all segments are modeled as equilibrium stages. The results from the initialization step are used to perform the rate based non-equilibrium calculations.

In this simulation process the Rate-Based Non-Equilibrium Model is used.

3.1.1 The rate-based modeling concept

Most models available for simulating and designing multi-component, multistage separation processes are based on the idealized concept of equilibrium or theoretical stages. This approach assumes that the liquid and vapor phases leaving any stage are in thermodynamic equilibrium with each other. The phase compositions, temperature, and vapor and liquid flow profiles are calculated by solving the governing material balances, energy balances, and equilibrium relations for each stage [14].

In practice, columns rarely operate under thermodynamic equilibrium conditions. Vapor-liquid equilibrium prevails only at the interface separating vapor and liquid phases. The separation achieved in a multistage column depends on the inter-phase mass and heat transfer rate processes. Multi-component mass transfer interactions can also have pronounced effects on the separation.

When the equilibrium approach is used to model a tray column, a correction factor (referred to as efficiency) attempts to account for the departure from equilibrium. Many definitions for efficiency exist, with wide variations in complexity and accuracy. In general, efficiencies depend on:

- Physical characteristics of the equipment, such as column configuration
- Hydrodynamics of the column
- Fluid properties of the system

Murphree vapor efficiencies are the most widely used. These efficiencies generally vary from stage to stage within a column, and from component to component. For multi-component systems, there are no theoretical limitations on Murphree efficiencies. Experimental evidence shows that component efficiencies:

- May vary strongly from component to component
- Can take any value including negative values

Methods used to calculate component efficiencies generally do not include the effect of the departure from thermal equilibrium.

Packed columns are also designed using the equilibrium stage concept. However, HETP is commonly used in place of efficiencies. HETP varies with:

- Type and size of the packing
- Hydrodynamics of the column
- Fluid properties of the system

Like efficiencies, HETPs may vary strongly from point to point within a column and from system to system.

RateFrac is based on a fundamental and rigorous approach. This approach avoids uncertainties that result when the equilibrium approach is used with estimated efficiencies or HETP. RateFrac directly includes mass and heat transfer rate processes in the system of equations representing the operation of separation process units. RateFrac:

- Describes the simultaneous mass and heat transfer rate phenomena
- Accounts for the multi-component interactions between simultaneously diffusing species

For nonreactive systems, RateFrac comprises:

- Mass and heat balances around vapor and liquid phases
- Mass and heat transfer rate models to determine inter-phase transfer rates
- Vapor-liquid equilibrium relations applied at interfacial conditions
- Correlations to estimate mass and heat transfer coefficients and interfacial areas

For chemically reactive systems, RateFrac includes equations to account for the influence of chemical reactions on heat and mass transfer rate processes. For systems involving equilibrium reactions, RateFrac includes equations to represent the chemical equilibrium conditions.

RateFrac completely avoids the need for efficiencies in tray columns or HETPs in packed columns. RateFrac has far greater predictive capabilities than the conventional equilibrium model.

3.1.2 Working with RateFrac

RateFrac is a rate-based non-equilibrium model for simulating all types of multistage vapor-liquid fractionation operations. RateFrac simulates actual tray and packed columns, rather than the idealized representation of equilibrium stages. RateFrac explicitly accounts for the underlying interphase mass and heat transfer processes to determine the degree of separation [14].

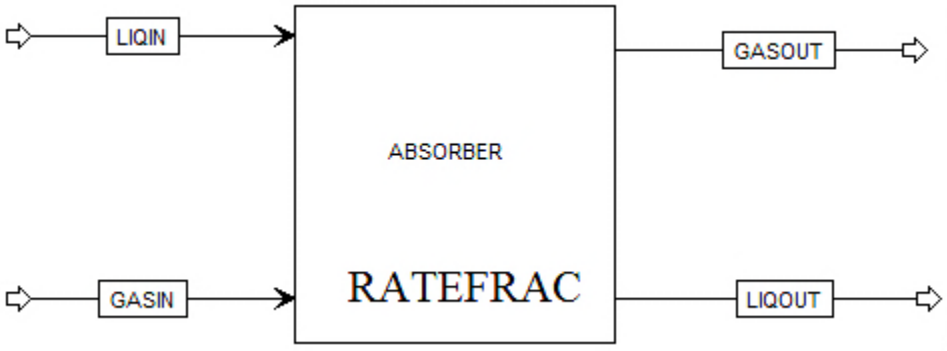

Figure-2 RateFrac model used in ASPEN PLUS simulator

RateFrac does not use empirical factors such as efficiencies and the Height Equivalent to a Theoretical Plate (HETP).

RateFrac is applicable for:

- Ordinary distillation
- Absorption
- Reboiled absorption
- Stripping
- Reboiled stripping
- Extractive and azeotropic distillation

RateFrac is suitable for:

- Two-phase systems
- Narrow and wide-boiling systems
- Systems exhibiting strong liquid phase non-ideality

3.2 Simulation of Liquid Solvent Absorption Process

To start the simulation process we have taken the composition of syngas as represented in Table3 [15]. The data were taken from a particular gasification process carried out at 750^{o}C (E/R=0.18, S/B=1.4) using pine bark as raw material [15].

Table-3 Composition of gas at the inlet of Absorption column

Gas Components	**Composition(% volume)**
Hydrogen(H_2)	31.4
Carbon Monoxide(CO)	20.6
Carbon Dioxide(CO_2)	35.3
Others(CH_4,C_2H_2,C_2H_4,C_2H_6,Air)	12.7

From the literature review it is clear that the CO_2 absorption efficiency of MEA is greater than any other amine solution. So we have taken MEA as our solvent. Different parameters like flow rate and temperature of solvent, gas flow rate, numbers of segments and pressure in the absorption column, were varied to test the effect on CO_2 absorption efficiency. Brief description and result of this study is given in the next section.

3.3 Experimentation on Solid Sorbent Absorption Process

In Chapter-2 (Literature Review) many alkali- alkaline materials are mentioned which can be used as an effective absorbent for CO_2 absorption. However we have taken CaO as our absorbent to carry out the experiment. The basic forward and backward reactions are as follows

$$CaO + CO_2 \rightarrow CaCO_3 \quad (3.1)$$

$$CaCO_3 \xrightarrow{HEAT} CaO + CO_2 \quad (3.2)$$

CaO specification:

The bed material used is extra pure and in powder form (Geldart Group C particle). The molecular weight is 56.08. The maximum percentage of different impurities is given below in Table-4.

Table-4 Absorbent Composition

Components/ Impurities/Characteristic	Maximum Limit (in %) present
Substance insoluble in HCl	0.10
Chloride (Cl)	0.05
Sulphate (SO_4)	0.50
Heavy Metals (as Pb)	0.01
Iron (Fe)	0.03
Loss on Ignition (800^0C)	10.0

3.3.1 Experimental set-up

We have taken a glass column clamped on a ply-wood board. A scale was fitted at one side of the board to measure the bed height. The top and bottom openings of the glass column were blocked with rubber cork. Small holes were drawn in the rubber corks to make passage for the inlet and outlet of gas stream. Narrow rubber pipes were fitted in the holes. The bottom pipe was connected to the outlet of the gasifier to admit the raw syn-gas. The top pipe was connected to the Gas Analyzer. Metal weir of very fine gauge was used to support the bed material. All the connections and joints were made air tight. 200g of CaO was taken inside the glass column to form an effective bed.

3.3.1.1 Gas Analyzer

The Gas Analyzer we have used is commercially known as Portable Gas Analyzer (Item Code: ACE 9000X-CGA). It can be used to measure the concentration of CO, CO_2, CH_4, H_2 and O_2 in sample gases simultaneously. For this an infrared sensing technology is introduced inside the Analyzer. The list count for concentration measurement is 0.01. Some of the special features of this Analyzer are automatic calorific value calculation, automatic zero calibration, built-in sampling pump [16].

3.3.2 Experimentation

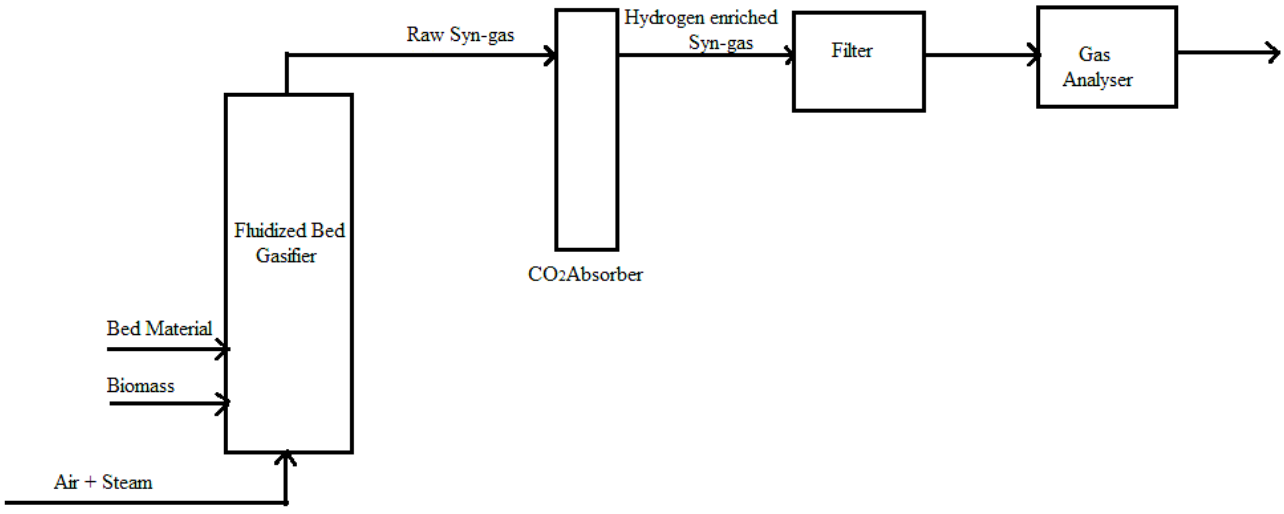

Figure-3 Complete flow sheet of gasification and purification process

The flow sheet for the complete gasification process and the purification is shown in Fig-3. Silica sand was used as bed material. The firing of the bed was initiated by burning LPG. When the desired temperature for the fluidized bed was achieved the flow of LPG was stopped. Then rice husk as biomass was then introduced into the hot fluidized bed and the gasification process was started. The gas coming out of the gasifier is referred as raw syn-gas and its composition was measured by the Gas Analyzer. At the same time the raw syn-gas was also passed through the absorber column (CaO- bed material) and the composition of the hydrogen enriched syn-gas was measured. When the raw syn-gas is passed through the bed the CO_2 present in gas reacts with CaO to form $CaCO_3$ (shown in reaction 3.1). As more and more gas was passed through the column, the bed becomes saturated and further absorption of carbon dioxide would not take place. Then the set-up was dismantled and the bed material was taken out and heated to a temperature more than 70^0 C where by the $CaCO_3$ gave away CO_2 to form CaO according to the reaction 3.2.

The absorption experiment was carried out for five different temperature, equivalence ratio and steam to biomass ratio. The composition of the gas (based on nitrogen and water free basis) before and after the absorption process was noted down. The result in tabulated form followed by brief discussion is given under the section Result and Discussion.

CHAPTER-4

RESULT AND DISCUSSION

The CO_2 absorption efficiency of mono-ethanolamine (MEA) was tested by simulation process through ASPEN PLUS simulator. Different parameters like solvent flow rate, temperature, and number of segments were varied and the result obtained were discussed below.

4.1. Variation in Solvent Flow Rate

The variation in composition of gas at the outlet of RateFrac model by varying solvent flow rates was observed through simulation process. For this purpose the number of segments and the temperature of solvent were held constant at 10 numbers and 303K respectively. The gas flow rate was fixed at 0.01953kmole/h and the absorber pressure at 1atm. The result obtained in the stream table of ASPEN PLUS simulator is represented in Table-5.

Table-5 Variation in outlet composition with change in solvent flow rate

Parameters Component gas	Inlet (% volume)	Outlet(% volume)			
		0.8kmole/h	1kmole/h	1.25kmole/h	1.5kmole/h
Hydrogen	31.4	40.1	43.2	47.5	50.5
Carbon monoxide	20.6	25.3	26.9	29.2	30.4
Carbon dioxide	35.3	19.1	13.5	5.6	0.6
Others	12.7	12.4	16.4	17.7	18.5

From the percentage of CO_2 at the inlet and outlet gas stream of the RateFrac model the CO_2 absorption efficiency of monoethanolamine (MEA) can be calculated. The result so obtained is shown Fig-4.

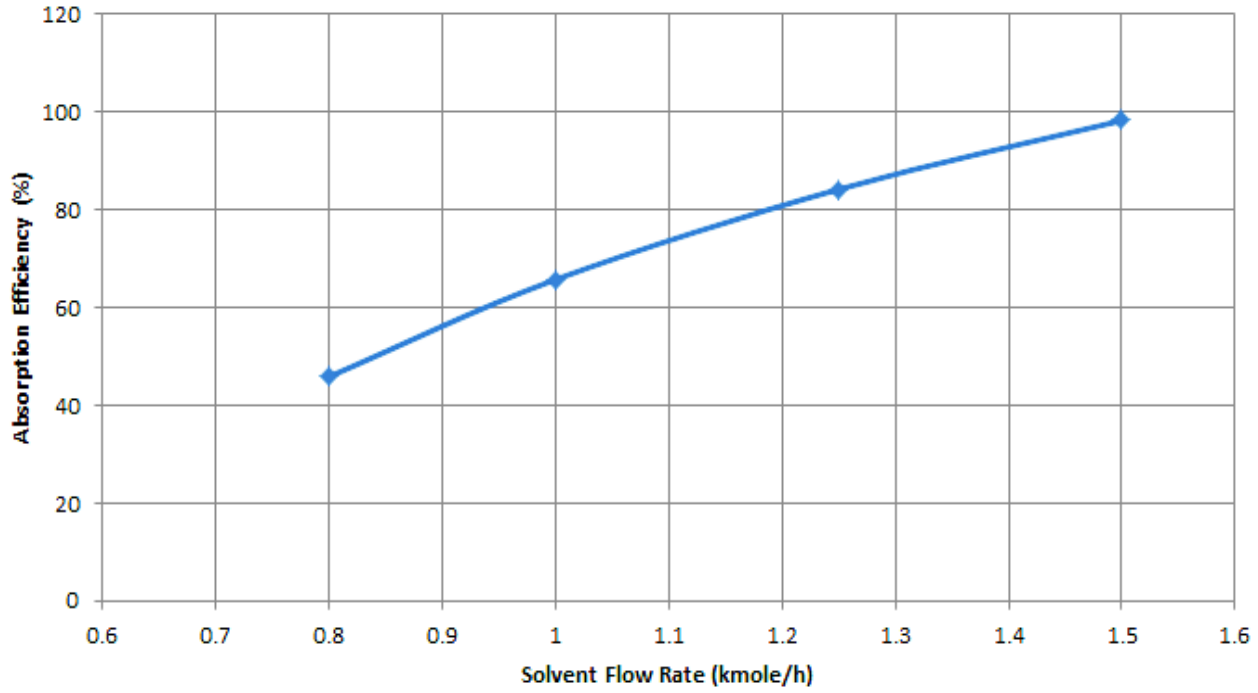

Figure-4 Variation of Absorption efficiency with solvent flow rate

4.2. Variation in Temperature of Solvent

To study the effect of variation in CO_2 absorption efficiency with a variation in solvent (MEA) inlet temperature the simulation process was carried out at constant number of segments (10 numbers) and constant solvent flow rate (1.25kmole/h). The gas flow rate and absorber pressure were fixed at 0.01953kmole/h and 1atm respectively. The composition of outlet gas so obtained at the stream table of ASPEN PLUS simulator is shown in Table-6.

Table-6 Variation in outlet composition with change in solvent temperature

Parameters Component gas	Inlet (% volume)	Outlet(% volume)			
		293K	303K	313K	323K
Hydrogen	31.4	50.4	47.5	43.4	40.7
Carbon monoxide	20.6	30.6	29.2	26.8	25.2
Carbon dioxide	35.3	0.4	5.6	13.4	18.7
Others	12.7	18.8	17.7	16.4	15.4

The absorption efficiency ~ temperature plot is shown in Fig-5.

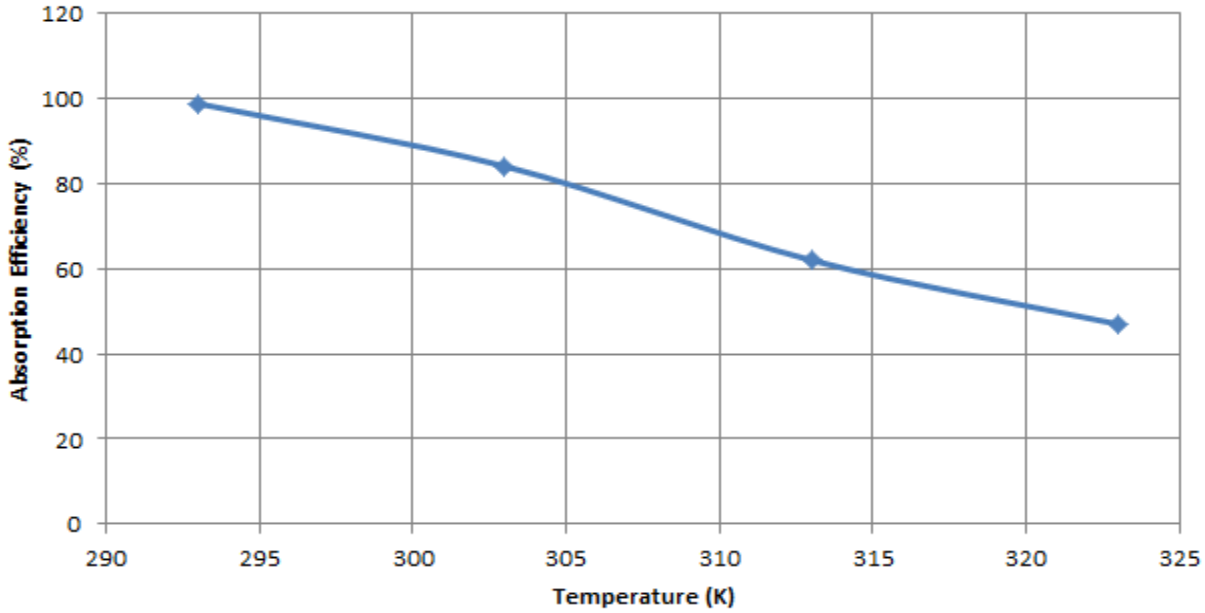

Figure-5 Variation of Absorption efficiency with solvent temperature

4.3. Variation in Number of Segments

At constant solvent flow rate (1kmole/h), gas flow rate (0.01953kmole/h), solvent temperature (303K) and absorber pressure of 1atm the number of segment in the RateFrac column was varied. The composition of the outlet gas stream so obtained with the help of ASPEN PLUS simulator is given in Table-7. Also a plot of Absorption efficiency ~ Number of segments is shown in Fig-6.

Table-7 Variation in outlet composition with variation in number of segments

Parameters Component gas	Inlet (% volume)	Outlet(% volume)				
		2	3	5	7	10
Hydrogen	31.4	40.9	42.0	42.9	43.1	43.2
Carbon monoxide	20.6	25.3	26.1	26.7	26.8	26.9
Carbon dioxide	35.3	18.3	16.0	14.2	13.7	13.5
Others	12.7	15.5	15.9	16.2	16.4	16.4

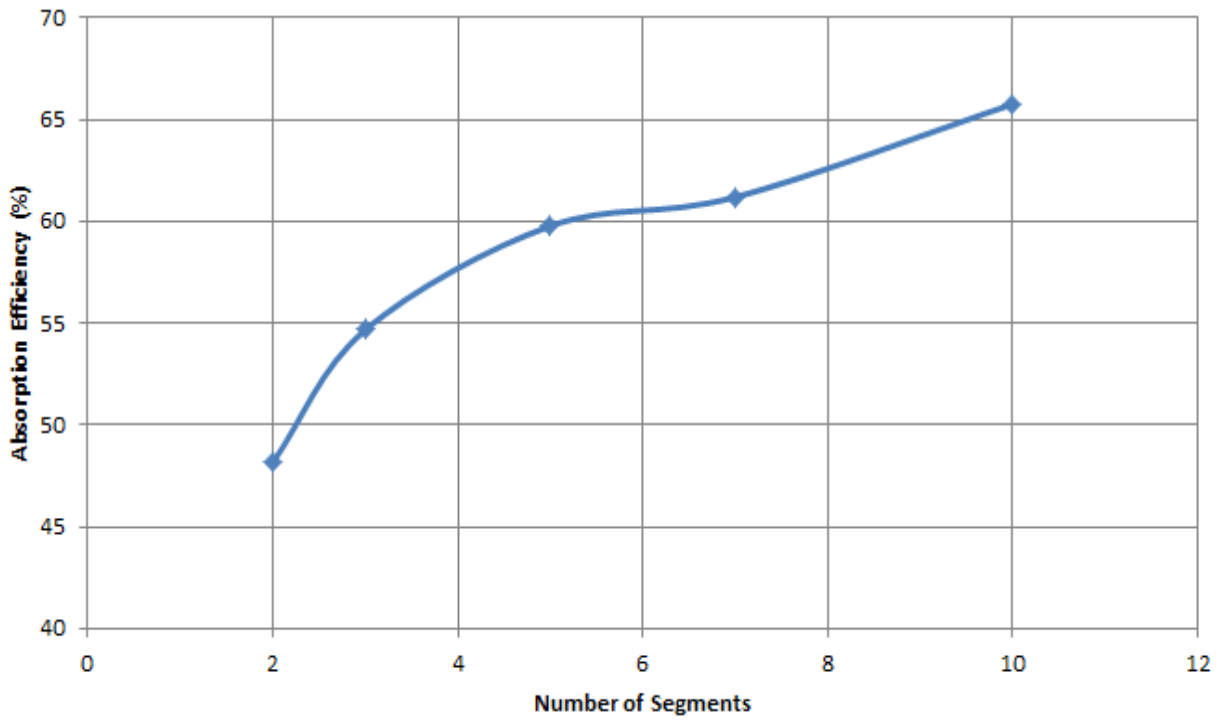

Figure-6 Variation of Absorption efficiency with variation in number of segments

4.4. Variation in Pressure inside the Absorber

For constant solvent and gas flow rate of 1kmole/h and 0.01953kmole/h respectively, solvent temperature (303K) and number of segments (10 numbers) the pressure inside the RateFrac column was varied and the result obtained was tabulated in Table8. A plot of Absorption efficiency ~ Pressure of absorption column is shown in Fig-7.

Table-8 Variation in outlet composition with variation in absorber pressure

Parameters Component gas	Inlet (% volume)	Outlet(% volume)				
		0.8atm	1.0atm	1.1atm	1.2atm	1.3atm
Hydrogen	31.4	40.1	43.2	44.8	46.6	48.4
Carbon monoxide	20.6	25.3	26.9	27.8	28.7	29.6
Carbon dioxide	35.3	19.1	13.5	10.4	7.2	4.0
Others	12.7	15.5	16.4	17.0	17.5	18.0

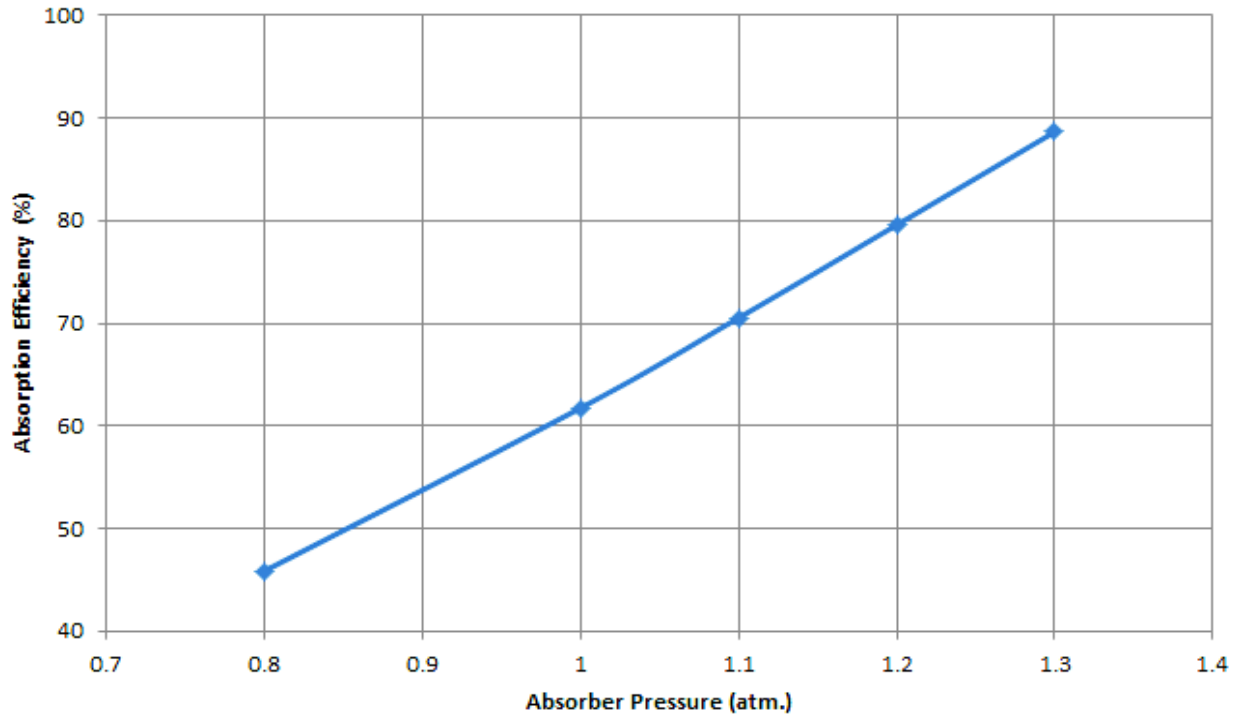

Figure-7 Variation of Absorption efficiency with absorber pressure

4.5. Variation in Gas Flow Rate

For constant solvent flow rate (1kmole/h), temperature of solvent (303K), number of segments (10 numbers) and pressure (1atm) inside the absorber the gas flow rate was varied. The results so obtained at the outlet of RateFrac column in ASPEN Plus simulator is tabulated in Table9. A plot of Absorption Efficiency ~ Gas flow rate is also shown in Fig-8.

Table-9 Variation in outlet composition with variation in gas flow rate

Parameters Component gas	Inlet (% volume)	Outlet(% volume)			
		0.017kmole/h	0.01953kmole/h	0.022kmole/h	0.025kmole/h
Hydrogen	31.4	45.7	43.2	41.4	39.9
Carbon monoxide	20.6	28.2	26.9	25.9	25.1
Carbon dioxide	35.3	8.9	13.5	16.8	19.6
Others	12.7	17.2	16.4	15.9	15.4

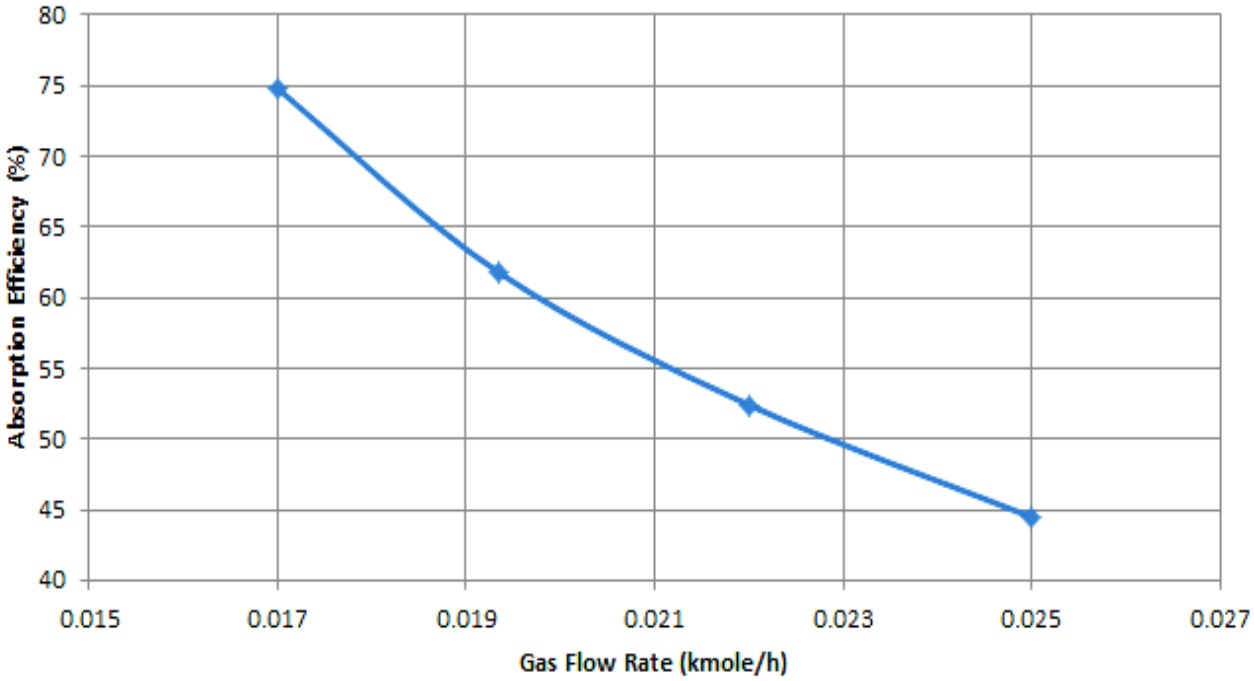

Figure-8 Variation of Absorption efficiency with Gas flow rate

In this work, the CO_2 absorption into monoethanolamine (MEA) solution has been investigated by simulation process through ASPEN PLUS simulator.

By increasing the solvent flow rate, the CO_2 absorption efficiency of MEA is increased as shown in the Fig-4. From Fig-4 it is clear that at a flow rate of 0.8kmole/h the absorption efficiency is only 46%. If we increase the flow rate to 1.0kmole/h and 1.25kmole/h the efficiency increases to 66% and 84% respectively. This result was expected, because greater flow rate implies greater amount of MEA, which will definitely absorb more CO_2 from the same gas stream. At first instant increasing the flow rate by 0.2kmole/h (from0.8kmole/h to 1.0kmole/h), the efficiency increases from 46% to 66%. But in the next increment (from 1.0kmole/h to 1.25kmole/h), increasing flow rate by 0.25kmole/h the efficiency goes to 84%. Thus greater increase in flow rate did not increase the efficiency in the same proportion. Finally as we go from 1.25kmole/h to 1.5kmole/h of solvent flow rate the efficiency goes from 84% to 98% only. Thus further increase in flow rate will not affect the efficiency significantly. This is because; the mass transfer from the gas phase to the liquid phase mainly depends upon the concentration gradient. With increasing flow rate the gradient tends to decrease and hence the mass transfer and absorption efficiency.

With an increase in temperature the solubility of CO_2 in MEA solution decreases. Hence the absorption efficiency of MEA decreases. From Fig-5 it is clear that at 293K the absorption efficiency of MEA is 99%. With continually increasing temperature the efficiency goes on decreasing. At a temperature of 323K it decreases to 47% keeping all other parameters constant. Thus one can conclude that the temperature has a strong effect on absorption efficiency of MEA solution.

A CO_2 absorption column is a unit where gas flow up and liquid (MEA solution) flows down. CO_2 is transferred from the gas phase to the liquid phase where it is absorbed by the amine solution. The gas and liquid phases are made to get in contact by the help of column plates or random or structured packing. Hence one can say that as the number of plates is increased there will be greater contact area and time of contact available for mass transfer to take place between the gas and liquid. Thus in our case the absorption of CO_2 will become more. From Fig-6 it is clear that as we are increasing the number of segments or plates the absorption efficiency of the amine solution is increasing as was expected. If we use 2 segments in the RateFrac column the absorption efficiency we are getting is only 48%. But if we increase the number of segments to 7 or 10 the absorption efficiency of MEA drastically increases to 61% and 67% respectively keeping all other parameters constant. It can also be observed that the rate of increase in absorption efficiency is lower than the increase in number of segments.

The absorption of CO_2 by MEA mainly depends upon the concentration gradient that is present between the gas phase and the liquid phase. From the ideal gas law it is clear that the concentration in the gas phase is directly proportional to the pressure of the gas. At higher absorber pressure the gas phase concentration is higher, which means the gradient available for the mass transfer is higher. From the Fig-7 it is clear that at an absorber pressure of 0.8atm the efficiency is only 46%, which increases to 89% if the column operates at a pressure of 1.3atm. Again from the graph (Fig-7.) it is clear that the rate of increase in efficiency is nearly linear with the rate of increase in absorber pressure. It was expected because; at this ambient pressure and temperature condition the CO_2 gas behaves as ideal gas.

By increasing the gas flow rate the absorption efficiency of MEA solution decreases. From the Fig-8 it is clear that at gas flow rate of 0.017kmole/h the absorption efficiency is 75%. If we increase the gas flow rate to 0.022kmole/h and 0.025kmole/h the absorption efficiency decreases

to 52% and 45% respectively. It was expected because; with an increase in gas flow rate the number of moles of CO_2 also increases, which would require greater amount of MEA to get absorbed. From Fig8 it is also clear that at initial stage the decrease in absorption efficiency is higher and the gradient decreases as we further increase the flow rate.

The simultaneous effect of the solvent flow rate and gas flow rate on absorption efficiency was studied next. For this purpose sixteen sets of data points had been generated with the help of ASPENPLUS simulator and were plotted on a three dimensional co-ordinate system as shown in Fig-9. For this purpose the help of the OriginPro 8 SRO v8.0724 (B724) software had been taken. The software itself had generated hundred data points (by cubic interpolation method) from the provided sixteen sets (forty eight numbers) of data points.

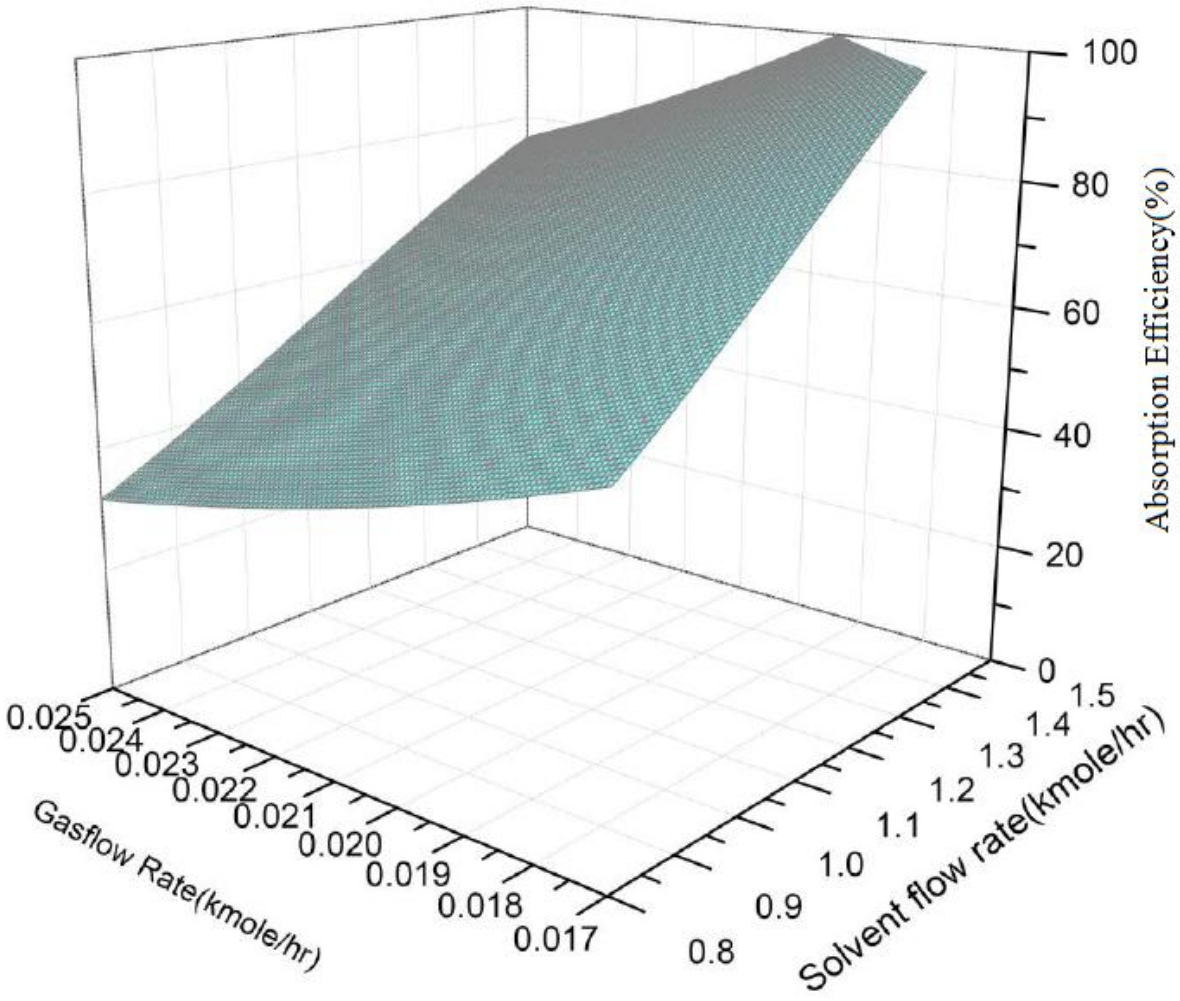

Figure-9 Simultaneous effect of Solvent and Gas flow rate on Absorption Efficiency of MEA

4.6 Solid Sorbent Absorption

The absorption of CO_2 by CaO is studied for different gasification condition like variation in temperature, equivalence ratio and steam to bio-mass ratio. The composition of the gas stream at the inlet and outlet of the absorber column is shown below in tabulated form. The calculations were done on nitrogen and water free basis. Hence the gas streams contain four main constituents like hydrogen, carbon monoxide, carbon dioxide and methane.

Table-10 shows the inlet and outlet gas stream composition for five different temperatures. Similarly the gas stream composition for variation in equivalence ratio and steam to biomass ratio is shown in Table11 and Table12 respectively.

Table-10 Inlet and Outlet gas stream composition with variation in Temperature

Temperature (^{0}C)	500	550	600	650	700
Components	Inlet Composition (volume %)				
H_2	28.73	33.16	36.34	37.89	43.58
CO	26.77	25.42	23.14	24.92	23.43
CO_2	36.26	34.26	32.19	29.08	25.62
CH_4	8.24	7.16	8.33	8.11	7.37
Components	Outlet Composition (volume %)				
H_2	34.04	39.97	40.63	41.61	47.30
CO	29.91	26.98	25.79	26.36	24.37
CO_2	26.79	25.15	24.48	23.22	20.31
CH_4	9.26	7.90	9.10	8.81	8.02

Table-11 Inlet and Outlet gas stream composition with variation in Equivalence Ratio

Equivalence Ratio	0.20	0.24	0.28	0.32	0.36
Components	Inlet Composition (volume %)				
H_2	44.81	43.86	38.10	34.14	26.60
CO	24.11	21.55	19.80	18.64	16.50
CO_2	22.97	27.25	34.66	39.88	49.63
CH_4	8.11	7.34	7.44	7.34	7.27
Components	Outlet Composition (volume %)				
H_2	48.71	47.01	42.47	38.80	31.69
CO	26.21	23.50	22.07	21.66	19.64
CO_2	16.22	21.45	27.13	30.98	40.02
CH_4	8.82	8.40	8.33	8.56	8.65

Table-12 Inlet and Outlet gas stream composition with variation in Steam to Biomass Ratio

S/B Ratio	0.50	0.75	1.00	1.25	1.50
Components	Inlet Composition (volume %)				
H_2	43.12	48.15	51.37	53.14	56.54
CO	21.91	20.15	16.02	11.98	7.35
CO_2	27.09	25.41	26.71	29.76	31.83
CH_4	7.88	6.29	5.90	5.12	4.28
Components	Outlet Composition (volume %)				
H_2	47.79	52.24	55.62	57.43	62.21
CO	23.73	21.86	17.32	12.94	7.96
CO_2	19.95	19.07	20.76	24.09	26.19
CH_4	8.53	6.83	6.30	5.54	4.64

For variation in temperature the steam to biomass ratio and the equivalence ratio were held constant at 0.5 and 0.25 respectively. For variation in equivalence ration the temperature and steam to biomass ratio were held constant at 700^0 C and 0.5 respectively. Similarly at constant temperature (700^0 C) and equivalence ratio (0.26) the variation of steam to biomass ratio was done.

The absorption efficiency of CaO found in our experiment is less than 30%. This is less than the expected efficiency. This discrepancy may be due to the following facts. The absorbent used was in powder form. Hence it comes under the Group C particles according to Geldart classification.

Group C particles are cohesive in nature. Normal fluidization are extremely difficult for these solids because inter particle forces are greater than those resulting from the action of gas. In small diameter beds they tend to rise as a plug of solids and in large diameter beds channels form from distributor to bed surface with no fluidization of solids [17].

Due to the improper fluidization the gas stream could not come in contact with the bed material properly. Hence the efficiency found was not up to the expectation.

CHAPTER-5

CONCLUSION

In this study we have investigated the CO_2absorption efficiency of MEA solution by simulation process. The RateFrac model in ASPEN PLUS simulator is used to study the rate-based non-equilibrium absorption process. From this study the following can be concluded.

The CO_2 absorption efficiency of MEA can be increased by increasing the flow rate of solvent in the column. Keeping all other parameters constant one can get more than 98% absorption efficiency of MEA solution.

With an increase in temperature of the solvent the absorption efficiency decreases. This can be attributed to the fact that with an increase in temperature the solubility of MEA decreases. For a particular condition having absorption efficiency of 47% at 323 K, can be increased to 84% and 99% by operating at 303K and 293K respectively.

By increasing the plates or number of segments the contact area as well as mass transfer between the gas and the liquid can be increased, resulting in greater absorption efficiency of solvent. For a fixed gas liquid counter current operation the efficiency can be increased from 48% with 2 numbers of segments to 67% by increasing the number of segments to 10.

Similarly by increasing the operating pressure of the absorber column the driving force for the mass transfer that is the concentration gradient between the gas phase and liquid phase can be increased and one can get higher absorption efficiency. For our particular case an absorption efficiency of 46% at 0.8atm operating pressure can be increased to 89% by increasing the pressure inside the absorber to 1.3atm.

By decreasing the gas flow rate the absorption efficiency can be increased. For a particular case of 44% absorption efficiency of MEA solution at 0.025kmole/h gas flow rate can be increased to 75% by decreasing the gas flow rate to 0.017kmole/h.

A study on simultaneous effect of variation in gas and solvent flow rate was also done and a comparative figure was plotted.

Also experiments on solid sorbent absorption using CaO as bed material were done for different gasification conditions.

For solid sorbent absorption the efficiency found was less than 30%. This is due to the powder form (Geldart Group C) of particles which are very difficult to fluidize because of channeling effect and improper distribution of gas stream. One of the ways of handling this type of particles is by introducing them to a bed of same material but of larger size.

Due to time constraint it could not become possible to study the variation of absorption efficiency of CaO with bed height, absorbent particle size.

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